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Effects of roughness on the wettability of high temperature wetting system

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ABSTRACT

The effects of substrate roughness on the wettability of non-reactive wetting and compound forming wetting systems were investigated by the sessile drop technique at high temperature. The AgCu eutectic alloy/copper and the AgCuTi/alumina wetting systems were selected. It is found that the substrate roughness has a great effect on both wetting systems. For the non-reactive wetting system, an additional capillary driving force exists when melt flows into the micro v-grooves of the rough surface, leading to a decrease in final contact angle (θ_f) and consequently a better wettability. For the compound forming metal/ceramic reactive wetting system, wetting on a rough surface exhibits a slow spreading kinetics and a short period of spreading time, and the retarding force of spreading increases because of overcoming the energy barriers due to asperities of the rough surface, resulting in an increase in θ_f. Thus, a rough substrate has negative effect on the wettability of the compound forming reactive wetting system.

1. Introduction

Wetting of a solid substrate by liquid metals and alloys at high temperature is of great technological importance in numerous metallurgical processes, for instance in hot dip metallic coating of steels, in soldering or brazing in microelectronics, and in metal/ceramic composites processing by infiltration routes [1–3]. Most practical solid surfaces are rough to some extent, and it is known for several decades that the wetting of a surface by a liquid is affected by its roughness, but early theoretical treatments are in conflict. Wenzel [4] believed that the additional surface of the rough surface causes an increase in its surface energy, and led to the prediction that

$$\cos\theta_R = W_R \cos\theta_0 \tag{1}$$

where W_R is the roughness area ratio (true area/nominal area), θ_R and θ_0 are the contact angles of sessile drops on rough and smooth surfaces respectively. Alternatively Shuttleworth [5] considered that the asperities on a rough surface could pose significant barriers to the flow of a liquid.

Most of the previous studies of wetting on rough surfaces focus on inert wetting at room temperature, and the liquid used mainly are water, glycerol, alcohol or silicon oil [6,7]. As for the spreading of molten metal at high temperature, the substrates are normally considered to be smooth, and only a few studies have investigated the wetting behavior of metal liquid on a rough surface [8,9]. Hitchcock [10] found that the rough surface is detrimental to high temperature wettability, such as in the Ni/SiO_2 and Cu/Ni system. Yost [11] and Rye [12] regarded the rough surface as a three-dimensional network of connected open capillaries or v-shaped grooves, through which liquid is drawn by capillary forces, and consequently, the rough surface leads to a better wettability, for example, in the SnPb/Cu system. Voytovych [13] found that the surface roughness has no significant effect on θ_f of the AgCuTi/alumina system. Thus, the effect of surface roughness on the equilibrium contact angle for high temperature wetting system is still not fully understood [14,15].

High temperature wetting systems can be broadly classified into three categories, viz., non-reactive wetting, dissolutive wetting and compound forming wetting systems [16]. A liquid metal spreading on a substrate with no reaction/dissolution is known as non-reactive or inert wetting, such as Pb/Fe, Sn/Mo and Sn/Ge systems [17]. Dissolutive wetting is defined as wetting accompanied by a significant dissolution of the solid in the liquid, such as Sn/Bi, Cu/Si and Ni/C systems [18–20]. For the compound forming wetting system, intermetallic compounds (IMCs) are formed at the solid/liquid (S/L) interface, such as in Sn/Au and AgCuTi/alumina systems [21]. It is known that the thermodynamics (driving force) and kinetics (spreading rate) are controlled by various factors for these wetting systems, so the effect of roughness on each system should be different.

This investigation focuses on a non-reactive wetting system and a compound forming metal/ceramic wetting system. The AgCu eutectic alloy/copper and the AgCuTi/alumina wetting systems were selected. The AgCu eutectic alloy is Cu-saturated at its melting point, so the AgCu eutectic/Cu system can be regarded as non-reactive wetting

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system. The AgCuTi/alumina system is a typical compound forming system. The driving force, wetting kinetics and interface chemistry for each system were studied, and the effects of roughness on non-reactive wetting and compound forming wetting were analyzed.

2. Experimental procedure

The liquid used in the wetting studies were AgCu eutectic alloy and AgCu–4.3 at.%Ti alloy. Purity Cu (99.99%) and commercial 96% pure polycrystalline alumina were selected as substrates. The surfaces of Cu and Al_2O_3 substrates were grinded by different grades of silicon carbide papers of varying grit sizes at random direction to obtain different surface roughness (R_a). R_a is the average deviation in height of random points on the surface from a line drawn through the trace such that the cross-sectional areas of asperities above and the grooves below are equal. The R_a value was measured using a surface roughness tester (Dektak150). Surface roughness values are an average of several independent measurements carried out on the substrate, and the error region for each sample is ± 10 nm. Before the experiments, the substrates were ultrasonic cleaned in acetone, and dried in a purified air blast.

Wetting experiments were performed by the sessile drop method in a high vacuum system (OCA15LHT-SV, DataPhysics Corporation, Germany). The furnace was equipped with windows enabling the melting and spreading processes to be filmed with a video camera (Zoom Xtender 1-51560, Navitar), which was connected to a computer and the recording speed is 20 frames per second. The video was automatically analyzed by a software (SCA 20. DataPhysics Corporation, Germany). Contact angles and linear dimensions of the drop were measured directly from the image of the drop section, with an accuracy of ±2° and ±2%, respectively. During the sessile drop experiment, a 50 ± 0.5 mg cylindrical solid metal was placed on a flat substrate inside the furnace, and they were heated in vacuum (10^{-4} Pa) at 5 K/min up to the holding temperature. The temperature is measured by a thermocouple in the heating chamber.

The holding temperatures for AgCu eutectic alloy and AgCu–4.3 at.%Ti alloy were 1060 K and 1200 K respectively. When the temperature reached its melting point, it takes several seconds for the cylindrical-shaped alloy gradually transformed into a regular spherical cap shaped melt, and the analysis system began to calculate the contact angle and the drop base radius at this moment ($t = 0$). After the wetting system reached its equilibrium, the samples were cooling with the furnace under vacuum condition.

After the sessile drop test, cross-section samples were made by cutting through the solder caps. Scanning electron microscopy (SEM) with associated energy dispersive spectroscopy (EDS) was used to characterize the substrate microstructure and reactive interface.

3. Results and discussion

3.1. Ag–Cu/Cu non-reactive wetting system

Fig. 1 shows the top view and spreading radius (r_f) as a function of roughness R_a for AgCu/Cu system at 1060 K. The surface roughness R_a of the different Cu samples are 16, 203, 337, 589, 664 and 887 nm respectively. It can be seen that the shape of spreading areas for each specimen is basically axisymmetric, and the spreading radius (r_f) increases drastically with the increase of roughness. The variation of R_a from 16 nm to 887 nm leads to an increase in the r_f from ~1.5 mm to ~11 mm. Moreover, the r_f obtained by image analysis exhibits a linear relationship with R_a. It should be pointed out that the r_f here means the radius of the total spreading area, which includes the drop base radius and the width of the precursor film.

Fig. 2 depicts the variations in contact angle as a function of time and roughness for the AgCu/Cu system at 1060 K. It can be seen from Fig. 2(a) that the contact angles of all samples drop sharply at the early stage (~1 s) of wetting. According to Eustathopoulos [22], the viscosity of AgCu molten metals is very low, and the rate of spreading for the non-reactive metal/metal system is controlled by viscous resistance, so the time needed for millimeter sized droplets to achieve capillary equilibrium in non-reactive systems is less than 10^{-1} s. Fig. 2(b) shows the changes of ultimate contact angle (θ_f) as a function of R_a. The AgCu eutectic alloy exhibits excellent wettability on a smooth copper substrate with the θ_f ~ 6°, and θ_f decreases gradually with the increase of R_a. With the roughness further increasing, θ_f tends towards a minimum angle of about 2°. It is well known that the measurement of contact angles less than 10° becomes difficult and the error increases as the angle approaches 0°, but taking into account the change of spreading area (Fig. 1a), it can be concluded that the rough surface enhances the wettability significantly in the non-reactive wetting system.

Fig. 3 shows the SEM images of the triple line region of the AgCu/Cu wetting system. In case of the smooth copper substrate with $R_a \approx 16$ nm (Fig. 3a), only a small amount of liquid flows along grain boundaries of the copper in front of the triple line. With the increase of R_a (Fig. 3b–d), the liquid metal flows in the network of micro v-grooves in front of the triple lines, and the flow distance increases with increasing roughness. Hence, for the non-reactive wetting system, the main difference between spreading on a smooth surface and a rough surface is the extensive flow of the liquid in the micro v-grooves.

3.2. AgCuTi/Al_2O_3 reactive wetting system

Fig. 4 shows the cross section and top view of the triple line region of the AgCu–4.3 at.%Ti/alumina wetting system holding at 1200 K for 1 h. During the wetting process, the reaction of Ti in AgCuTi and the Al_2O_3 substrate leads to the formation of a interfacial product layer with a

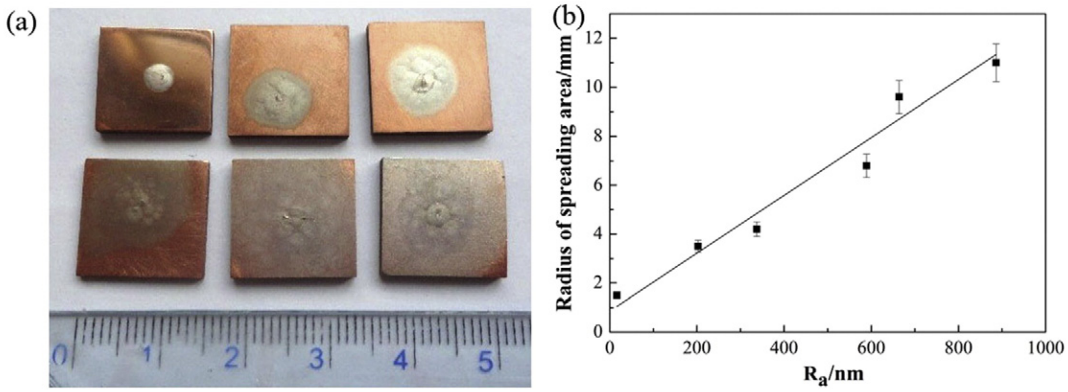

Fig. 1. Top view and spreading radius as a function of roughness R_a for the Ag–Cu eutectic/Cu system.